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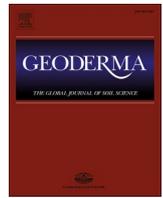
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Role of soil minerals on organic phosphorus availability and phosphorus uptake by plants

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ABSTRACT

Organic phosphorus (OP) represents a significant fraction of the total P pool in soils. With the increasing use of organic resources to substitute mineral P fertilizers and the need to recover P from the soil, it is pivotal to gain insight into the interactions between various OP forms and soil minerals and their consequences on P availability. Here, we aim at elucidating the extent to which OP compounds adsorbed onto major soil minerals may be available to plants. Ryegrass (*Lolium multiflorum*) plants were grown in RHIZOtest devices in the presence of OP including myo-inositol hexakisphosphate (IHP), glycerophosphate (GLY), and glucose-6-phosphate (G6P) and inorganic P (IP) compounds that were previously adsorbed onto Fe and Al oxyhydroxides (goethite and gibbsite, respectively) and clay minerals (montmorillonite and kaolinite). Phosphorus availability and P uptake were then determined through rhizosphere and plant characterization. Irrespective of the type of mineral, ryegrass was able to take up about 3–18 % of adsorbed OP compounds. The magnitude of availability and uptake depended on the OP compounds and the type of soil minerals. The potential availability of OP adsorbed by different minerals was strongly mediated by mineral-OP interaction types and properties. The P uptake increased in the following order: kaolinite-OP \ll gibbsite-OP \leq goethite OP \ll montmorillonite-OP. Phosphorus uptake from adsorbed OP compounds showed contrasting patterns compared to adsorbed IP and depended more on available P concentration in the rhizosphere rather than on the binding strength of OPs to the mineral surface.

1. Introduction

Phosphorus (P) is a limiting nutrient in both natural and agricultural ecosystems due to its strong sorption with soil particles which limits its availability for plants (Fan et al., 2020; Hou et al., 2020). The depletion of the world's phosphate rock reserves used to produce mineral fertilizers threatens food security (Filippelli, 2008; Reijnders, 2014; Yu et al., 2022). Recycling P from organic input becomes thus a necessity for sustainable P management in agroecosystems (Elser and Bennett, 2011; Houben et al., 2017; McGrail, 2021). However, P contained in organic input and soil occur under various inorganic and organic forms that differ in their availability to plants (Faucon et al., 2015; Kahiluoto et al., 2015). The predominant organic P (OP) forms in organic input include myo-inositol hexakisphosphate (IHP), glycerophosphate (GLY) and, glucose-6-phosphate (G6P) (Giles et al., 2011; Vincent et al., 2013). Each compound differs from the others in its P content, type of P bond, and size of the molecule (Amadou et al., 2021; Xu and Arai, 2022). These biochemical properties are likely to impact the availability of OP forms to plants as they govern their interactions with the solid phases. Most

research on the fate of P applied to soil has focused on inorganic P (IP) compounds, showing that most of it is adsorbed at the surface of soil particles, which in turn influences its availability to plants (Grenon et al., 2021; Hinsinger, 2001; Houben et al., 2011). In contrast, the dynamics of OP forms and their availability have been understudied to date and the contribution of these compounds to plant nutrition is poorly known (Faucon et al., 2015; Haygarth et al., 2018; Mezeli et al., 2019).

Soil minerals such as iron (Fe) and aluminum (Al) oxyhydroxides (e.g. goethite and gibbsite, respectively) and clay minerals (e.g., kaolinite, montmorillonite) are major components of soils (Xu and Arai, 2022). They have received considerable attention due to their high P adsorption capacity (Bortoluzzi et al., 2015; Ryan et al., 2001; Xu et al., 2021) which may cause an OP utilization efficiency in soils as low as 5–10 % (He et al., 1994). This leads to poor utilization of OP sources in agroecosystems (Amadou et al., 2021; Sulieman and Mühling, 2021). Organic P compounds adsorbed on minerals were found to be the most stable P forms in different soil types (Martin et al., 2002; Montalvo et al., 2015). This has been attributed to their specific binding mechanism.

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Indeed, it was found that the number of the phosphate groups in a certain OP compound determines the stability of its complex with the mineral surface (Anderson and Arlidge, 1962; Li et al., 2021). For instance, IHP with its six phosphate groups generally exhibits a strong binding and high stability as compared with other OP or IP compounds which have a smaller number of phosphate groups (Gerke, 2015). Ognalaga et al. (1994) showed that up to four phosphate groups of IHP interact with the goethite surface, leading to the formation of inner-sphere complexes between the IHP phosphate groups and the goethite surface. A similar mechanism has been suggested for other P-mineral complexes. Desorption of P from mineral surfaces would be more limited for OP compounds compared to IP (Bai et al., 2021; Gerke, 2015; Ruttenberg and Sulak, 2011). However, the extent to which OP compounds adsorbed to soil minerals can desorb remains poorly known and their availability to plants is still debated.

Several authors have suggested that the mineral-OP bridging compounds are not available to plants because these complexes are formed during the slow reaction phase with soil minerals (Hingston and Quirk, 1974; Barrow and Shaw, 1975). This process has been hypothesized to be a major cause of plant growth limitation (Javaid, 2009). After several desorption cycles, Martin et al. (2002) found that 20 % of IP desorbed from goethite while it only accounted for less than 5 % for IHP. Similar findings were reported by Ruyter-Hooley et al. (2015) with limited desorption of IHP (<3% of total amount) on gibbsite, even in the presence of humic acids as competing ligands for sorption sites. In addition, Gerke (2015) proposed that the presence of Ca in soil solution further reduces IHP solubility and availability due to the formation of Ca-IHP precipitates. These studies suggest that the availability of OP is probably mainly limited by its solubility and not by enzymatic activity (Gerke, 2015; Lung and Lim, 2006). This is corroborated by plant growth tests in the presence of synthetic goethite (Martin et al., 2002) and in P-fixing soils (Adams and Pate, 1992) where sorption and/or precipitation also lowered both IHP solubility and availability. In any case, there was a greater affinity of the OP compounds for soil minerals than that of the IP compounds, indicating the formation of a very stable complex of OPs with mineral surfaces. Thus, it can be expected that desorption and plant availability of mineral-OP complexes are lower than those of IP compounds. However, the very few studies on OP do not adequately quantify their potential contribution to P availability in the organic fertilizer-soil-plant system (Amadou et al., 2021; Klotzbücher et al., 2020; Sulieman and Mühling, 2021). For example, although some studies consider IHP as a source of available P, its availability in the presence of the major soil minerals remains poorly understood (García-Lopez et al., 2015; Martin et al., 2002). Moreover, these studies did not consider other important P pools such as GLY or G6P which, together with IHP, nevertheless represent an important part of the total P in the soil (Darch et al., 2014; Gérard, 2016). Furthermore, the soil minerals used were in most cases goethite while Al oxyhydroxides and clays were much less considered (Amadou et al., 2022; Gérard, 2016). To our knowledge, there are no study that evaluates and compares the availability of P to plants from the major OP compounds (IHP, GLY, and G6P) that were adsorbed onto the major soil minerals (Fe and Al oxyhydroxides and clay minerals). It is therefore crucial to understand the complex mechanisms that control the dynamics of important compounds of OP in major soils fertilized with organic inputs and the efficiency of the OP-minerals interaction in supplying P to crops.

Overall, our understanding of the dynamics of the major OP pools in the soil-plant system is very limited. Most research has focused on the dynamics of IP forms (Sulieman and Mühling, 2021), suggesting that soil characteristics control their availability to plants (Gómez-Suárez et al., 2020). However, OP forms may strongly differ from each others and have therefore different biogeochemical processes controlling their availability and uptake by plants (Amadou et al., 2021; Condon et al., 2005). To date, it is not known how the chemical forms of OPs, and their interactions with soil minerals, influence the uptake of OPs by plants in ecosystems. The paucity of research significantly limits our ability to

understand the overall dynamics of P cycling in ecosystems and to optimize the use of renewable P fertilizers which often contain various forms of OP (Kelessidis and Stasinakis, 2012; Mininni et al., 2015). The goal of this study was to elucidate the extent to which OP bound to Fe and Al oxyhydroxides and clay minerals complexes contributes to plant P acquisition. This could open up possibilities for the use of renewable nutrient-rich organic amendments according to different soil mineral properties. Specifically, we determined the plant P availability from several complexes of IHP, G6P, and GLY that were adsorbed onto Fe and Al oxyhydroxides (goethite and gibbsite) and clay minerals (kaolinite and montmorillonite). Mineral-IP complexes with KH_2PO_4 were also carried out for comparison. The P uptake for each compound was determined using ryegrass grown in an RHIZOTest device. The three main following hypotheses were addressed: (1) P from adsorbed OP compounds is available to ryegrass and varies with soil mineral properties; (2) the relative P uptake of the different complexes OP-minerals are dependent on their binding strength and (3) adsorbed OP compounds are less available than adsorbed IP because it desorbs less and requires not only desorption but also enzymatic cleavage before being taken up by ryegrass.

2. Materials and methods

2.1. Organic P compounds and individual soil minerals

Three OP compounds, including myo-inositol hexakisphosphate (IHP), glycerophosphate (GLY) and glucose-6-phosphate (G6P), and one inorganic P (KH_2PO_4) were selected for experiments. Organic P compounds were initially selected based on their predominance in organic inputs and soils, the types of P bonds and their different molecular sizes. The inorganic P form was chosen for comparison with organic P compounds. Four minerals were selected to be representative of the predominant minerals in soils: Goethite [$\text{Fe}(\text{OH})\text{O}$] and gibbsite [$\text{Al}(\text{OH})_3$] were chosen as representative of Fe and Al oxyhydroxides; kaolinite and montmorillonite were selected as clay minerals, particularly 1:1 phyllosilicate and 2:1 phyllosilicate respectively. All mineral powders were obtained from Sigma-Aldrich Chemie and VWR (France) for experimentation.

2.2. Preparation of minerals-P adsorption complexes

The four soil minerals were loaded with the three OP compounds or inorganic P to serve as a P source for ryegrass. Solutions containing 1 g P/L in 0.1 M KCl at pH 5.5 were prepared using the different P compounds. Goethite, gibbsite, kaolinite, and montmorillonite was weighed in portions of 100 g into 1-L bottles. Then, 200 mL of 0.1 M KCl were added and the bottles were shaken for 24 h at 25 °C to sufficiently hydrate the adsorption sites on the minerals. The pH was maintained at 5.5 ± 0.05 by adding 0.1 M HCl or NaOH solution. To start the formation of OP-mineral complexes, each of the 1 L bottles containing the soil minerals was filled with 800 mL of each P solution. In each bottle containing both the soil minerals and P compounds, some drops of hexanol were added to suppress microbial activities. Bottles were shaken on a mechanical shaker for 24 h at 25 °C and then centrifuged (3000 G for 15 min). The 1 L bottles were distributed into several 250-mL bottles, centrifuged, and the supernatants were collected and removed. The produced P-loaded minerals were agitated in deionized water and frozen at -20 °C. To determine the amounts of adsorbed P, a certain volume of supernatants was immediately filtered through a 0.22- μm membrane syringe filter for P analysis. The concentration of P in the supernatants was determined colorimetrically (Ohno and Zibilske, 1991) after hydrolyzing OP to IP using the persulfate oxidation method (Peters and Van Slyke, 1932). The quantity of P adsorbed was calculated as the difference between the initial amount of P added and the remaining P amount in the supernatant at the end of the experiment. Total P concentration in a subsample of each P-loaded was also determined using

the procedure by Ostrofsky (2012) and showed very similar values compared to the ones determined as the difference between the initial and the final P amount in the supernatant (differences were in the range of 3–5.5 % for the organic mineral-P complexes and 1.5–5 % for the inorganic mineral-P complexes). The P loadings of the mineral-P complexes produced are shown in Table 1. All minerals were loaded to reach their adsorption maxima.

2.3. Characterization of OP desorption

The desorption ability of various P compounds from soil minerals was characterized using a 0.1 M KCl extraction. Briefly, 40 mL of 0.1 M KCl adjusted to pH 5 were added to 0.5 g minerals-P complex. Samples were then shaken on a mechanical shaker at 25 °C for 24 h. After centrifugation for 10 min, 5 mL of the supernatant was taken for the measurement of desorbed P concentration by colorimetry (Ohno and Zibilske, 1991). In addition, we carried out two additional desorption steps by successively desorbing P at 48 h and 72 h using the same extractant to further characterize the desorption dynamics of the P forms.

2.4. Experimental setup and plant growth

We used the RHIZOtest device (MetRHIZlab, France) (Fig. 1) designed by Bravin et al. (2010) which consists in separating plant roots from soil with a 30-mm polyamide mesh to facilitate the collection of roots and rhizosphere (Houben and Sonnet, 2015). As described by Gómez-Suárez et al. (2020), in a first step (preculture period), 0.20 g of ryegrass (*Lolium multiflorum*) seeds were grown for 14 days in hydroponics in a cylinder closed at the bottom with a 30 µm polyamide mesh allowing the development of a dense, planar root mat with a nutrient solution: Ca(NO₃)₂ (2 mmol/L), MgSO₄ (0.5 mmol/L), K₂SO₄ (0.7 mmol/L), KCl (0.1 mmol/L), KH₂PO₄ (0.1 mmol/L), MnSO₄ (0.5 µmol/L), CuSO₄ (0.5 µmol/L), ZnSO₄ (0.5 µmol/L), (NH₄)₆Mo₇O₂₄ (0.01 µmol/L) and Fe-EDTA (100 µmol/L). After this preculture period, 15 plants were removed from the experiment and the roots and shoots were kept for analysis to determine the amount of P in plants before the cultivation period.

In a second phase (cultivation period), the two-week-old seedlings, showing a dense root mat, were transferred to a thin layer of substrate made of different mineral-P complexes previously prepared and acid-

washed quartz. Prior to the experiment, the substrates were sterilized by autoclaving at 121 °C for 2 h (Gómez-Suárez et al., 2020) to eliminate potential microorganisms, allowing therefore to attribute the results to the only effect of root activity. To avoid any P limitation for plants during the experiment, we supplied a total amount of P which was previously found to sufficiently meet the plant requirement in such RHIZOtest devices (Gómez-Suárez et al., 2020). Thus, the amount of mineral-P complex added to the mixture was calculated to supply 40 mg of P in each treatment while the amount of quartz was calculated to reach a final mass of 10 g, which corresponded to a 1.5-mm thick soil layer. The soil layer was then connected to a 500 mL nutrient solution with a filter paper wick. The composition of this nutrient solution was the same as that used for the preculture period except that P was not added. The RHIZOtest devices were placed in controlled conditions (phytotron) under a photoperiod of 12 h, constant temperature (25 °C), and relative humidity (80 %). Unplanted control treatments, in which the quartz - mineral-P complex had been incubated in similar devices without plants (hereafter called the bulk substrate), were also conducted. In total, 128 such devices were implemented: 4P compounds (IHP, GLY, G6P, and IP) × 4 soils minerals (goethite, gibbsite, kaolinite and montmorillonite) × 2 crop conditions (ryegrass and bulk soil) × 4 replicates.

2.5. Plant sampling and analysis

The plants were harvested after 15 days of contact with mineral-OP complexes. At harvest, shoots and roots were separated and roots were gently rinsed with deionized water. Shoots and roots were then dried at 60 °C for 72 h, weighed, and crushed before analysis. The concentration of P in shoots and roots was determined colorimetrically (Ohno and Zibilske, 1991) after mineralization by 65 % HNO₃ digestion directly in a microwave Teflon vessel (Lange et al., 2014). The amount of P taken up by shoot and root from the P-mineral complexes was calculated as the difference between the amount of P in plant parts at the end of the experiment minus the average amount of P in plants at the end of the preculture period. Total plant P uptake from P-minerals was calculated by summing P uptake from P-minerals by roots (i.e., root P concentration multiplied by root dry mass) and P uptake from P-minerals by shoot (i.e., shoot P concentration multiplied by shoot dry mass). The percentage of P recovered by ryegrass was determined by the following equation:

$$P \text{ recovered (\%)} = \frac{\text{Amount of P uptake per pot (mg P)}}{40 \text{ (Amount of P supplied per pot, mg P)}} * 100$$

2.6. Rhizosphere and bulk soil analyses

The availability of P in the rhizosphere and the bulk soil collected at the end of the RHIZOtest experiment was assessed by anion exchange membrane (Nobile et al., 2019). Briefly, 0.5 g (mineral-P + quartz) of the collected mineral-P complexes were added to 50 mL bottles with 30 mL deionized water and two strips of anion exchange membrane. The whole set was mixed and stirred for 16 h. The membranes were then removed and rinsed in deionized water and the P recovered by shaking for 1 h in 20 mL of 0.5 M HCl. Phosphorus concentrations were analyzed by colorimetry using a spectrophotometer (610 nm). Just after the harvest, alkaline phosphatase activity in the rhizosphere was determined by measuring the amount of p-nitrophenol (PNP) released from the addition of 5 mM p-nitrophenyl phosphate according to Tabatabai and Bremner (1969).

2.7. Data processing and analysis

Data were statistically analyzed with R software (R version 4.1.3). The impact of factors (P compounds, soil minerals, and their combined effect) on P availability and uptake was modeled by generalized linear

Table 1

P adsorption capacity of the produced minerals-P adsorption complexes. Go: goethite; Gib: gibbsite; K: kaolinite; M: montmorillonite; IP: inorganic P; IHP: Myo-inositol hexakisphosphate, GLY: glycerophosphate and G6P: glucose-6-phosphate.

Mineral-P complexes	Quantity of P adsorbed (µg/g)
Go-IP	2810
Go-IHP	3742
Go-GLY	1398
Go-G6P	4337
Gib-IP	20949
Gib-IHP	56698
Gib-GLY	6237
Gib-G6P	5588
K-IP	1736
K-IHP	6082
K-GLY	1222
K-G6P	2295
M-IP	3709
M-IHP	4857
M-GLY	1045
M-G6P	2338

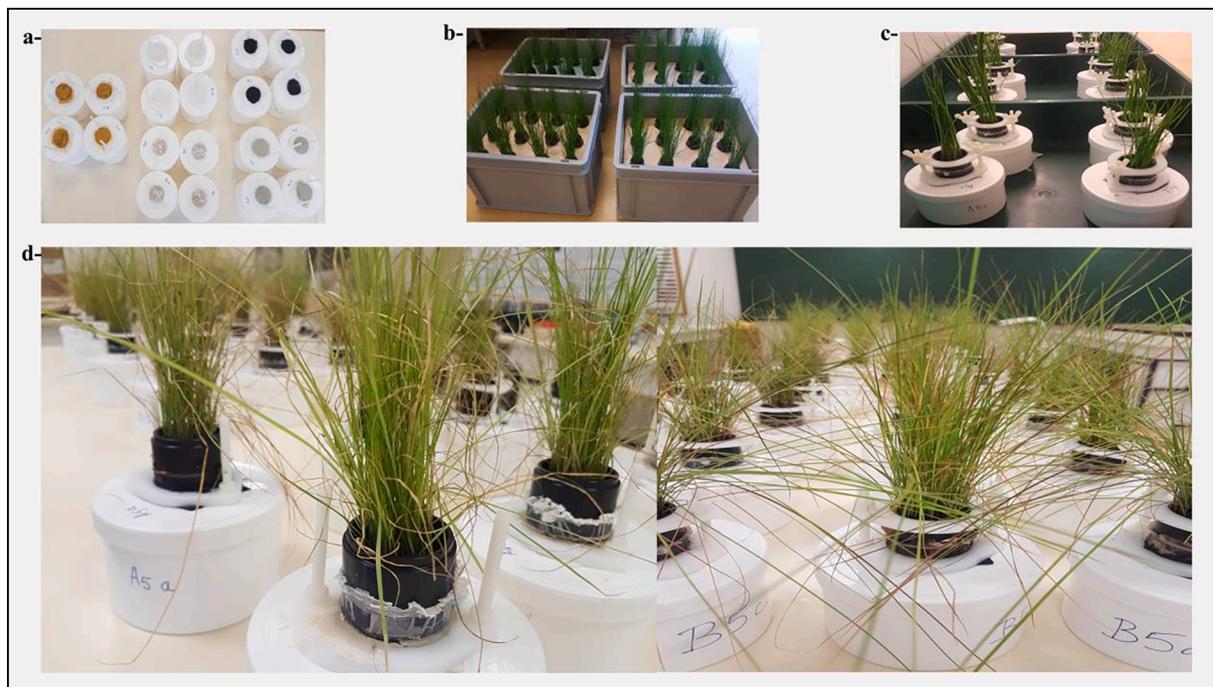


Fig. 1. Picture of the experimental Setup and Plant growth using the RHIZOtest device: a- soil layer of quartz - mineral-OP complex; b- preculture period; c- contact between the soil and plant device; d- result at the end of the experiment.

models (GLM) using the “FactomineR” package. The GLM model was used to avoid mathematical transformation of the variables and to get rid of the strict assumption that “the residuals will follow a conditionally normal distribution” (McCullagh and Nelder, 2019; Warton et al., 2016) and allow the use of a variety of other distributions of the exponential family for the residuals (Cohen et al., 2014). All factors were tested individually and the models were compared based on second-order Akaike information (AICc), with the lowest relative value being considered the best fit. The ANOVA of the best-fit GLM model with a chi-square test generated the deviance analysis table that gave the significance level of all factors. Statistical analyses to compare the average results of percent P recovered, enzyme activities, and biomass were performed using a one-way analysis of variance (ANOVA) followed by Tukey’s honest significant difference (HSD) test ($p < 0.05$).

3. Results

3.1. Biomass production

Total biomass varied slightly between treatments (Table 2). Although there was a significant difference between goethite and gibbsite for IHP forms, total biomass did not vary significantly between treatments. Some weak differences were observed between soil mineral types. The lowest biomass was observed with the Gib-OP complex and the highest with the K-OP complex. In general, except on gibbsite, the mineral-OP complexes produced equal or slightly more total biomass than the mineral-IP complexes.

3.2. Combined effects of organic P and soil minerals on P uptake

The impact of P compounds, soil minerals, and their combined effect on total P uptake by ryegrass was modeled by GLM (Table 3). Variations in P uptake by ryegrass were significantly affected by P compounds and their interaction with soil minerals. As shown by the lower AIC values (Table 3), the variation was more dependent on the interaction between minerals and P compounds. During the growing season, P recovered by ryegrass was 21–28 % from adsorbed IP, 0–5 % from adsorbed IHP,

Table 2

Effect of different P-mineral complexes on the root, shoot, and whole plant biomass (root + shoot biomass). Results are mean \pm standard error. Means with a different letter were significantly different according to Tukey’s HSD test at $P < 0.05$. Comparisons of means were made for each mineral category. Soil minerals (Go: goethite, Gib: gibbsite, K: kaolinite, and M: montmorillonite); Phosphorus compounds (IHP: Myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate, and IP: KH_2PO_4); Dashes (-) identify mineral-phosphorus complexes produced by adsorption of forms of P onto soil minerals. The example Go-IHP refers to goethite and Myo-inositol hexakisphosphate complexes.

	Root Biomass (g)	Shoot Biomass (g)	Total Biomass (g)
Go-IP	0.27 \pm 0.01 a	0.55 \pm 0.10 a	0.82 \pm 0.11 a
Go-IHP	0.27 \pm 0.03 a	0.85 \pm 0.11 b	1.12 \pm 0.13 b
Go-GLY	0.33 \pm 0.03 a	0.64 \pm 0.09 ab	0.96 \pm 0.12 ab
Go-G6P	0.27 \pm 0.09 a	0.54 \pm 0.09 a	0.81 \pm 0.19 ab
Gib-IP	0.26 \pm 0.03 a	0.60 \pm 0.12 a	0.86 \pm 0.16 a
Gib-IHP	0.17 \pm 0.09 a	0.42 \pm 0.16 a	0.60 \pm 0.25 a
Gib-GLY	0.19 \pm 0.03 a	0.43 \pm 0.08 a	0.62 \pm 0.12 a
Gib-G6P	0.21 \pm 0.01 a	0.45 \pm 0.06 a	0.66 \pm 0.07 a
K-IP	0.22 \pm 0.03 ab	0.83 \pm 0.15 a	1.05 \pm 0.15 a
K-IHP	0.18 \pm 0.02 a	0.61 \pm 0.14 a	0.79 \pm 0.16 a
K-GLY	0.28 \pm 0.01 c	0.85 \pm 0.19 a	1.13 \pm 0.20 a
K-G6P	0.27 \pm 0.004 bc	0.75 \pm 0.13 a	1.02 \pm 0.13 a
M-IP	0.21 \pm 0.03 a	0.72 \pm 0.09 a	0.93 \pm 0.12 a
M-IHP	0.19 \pm 0.04 a	0.68 \pm 0.15 a	0.87 \pm 0.20 a
M-GLY	0.23 \pm 0.02 a	0.72 \pm 0.20 a	0.95 \pm 0.22 a
M-G6P	0.27 \pm 0.09 a	0.71 \pm 0.06 a	0.98 \pm 0.19 a

4–18 % from adsorbed GLY, and 2–9 % from adsorbed G6P, depending on the mineral type (Table 4).

3.3. Effect of OP compounds on P uptake by ryegrass

Except for kaolinite, P uptake by ryegrass varied significantly

Table 3

The GLM model results testing the impact of factors (P compounds, soil minerals, and their combined effect) on total P uptake.

Variables effects	P uptake <i>p</i> -value	AIC
P forms	<0.001	268–329
Minerals: P forms	<0.001	156–199
Soil minerals	<0.001	314–388
R ²	0.92	

Table 4

Effect of different P-mineral complexes on the percentage of P recovered by ryegrass from adsorbed OP compounds. Results are mean ± standard error. Means with a different letter were significantly different according to Tukey's HSD test at $P < 0.05$. Comparisons of means were made for each mineral category. Soil minerals (Go: goethite, Gib: gibbsite, K: kaolinite, and M: montmorillonite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate, and IP: KH₂PO₄); Dashes (-) identify mineral-phosphorus complexes produced by adsorption of forms of P onto soil minerals. The example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

Mineral-P complexes	P recovered by ryegrass (%)
Go-IP	21 ± 1.62 d
Go-IHP	1 ± 0.08 a
Go-GLY	11 ± 0.62 c
Go-G6P	4 ± 0.62 b
Gib-IP	3 ± 1.09 b
Gib-IHP	0 ± 0.01 a
Gib-GLY	9 ± 1.66 c
Gib-G6P	3 ± 0.39 b
K-IP	22 ± 3.97 b
K-IHP	4 ± 0.61 a
K-GLY	4 ± 0.32 a
K-G6P	2 ± 0.18 a
M-IP	28 ± 2.37 c
M-IHP	5 ± 1.05 a
M-GLY	18 ± 2.70 b
M-G6P	9 ± 2.58 a

between the adsorbed OP compounds (Table 5; Fig. 2). Differences in total P uptake between OP compounds decreased in the order GLY >> G6P > IHP (Table 4; Fig. 2). Phosphorus concentrations in roots and shoots were higher in the presence of adsorbed GLY compound compared to the other OP compounds (Table 4). Of all OP compounds, adsorbed IHP was the lowest supplier of P to ryegrass. Compared to IP, P uptake from adsorbed OP compounds was highly contrasted and dependent on the specific compounds of OP. Phosphorus uptake from adsorbed IHP and G6P was significantly lower than that from adsorbed IP, with the order being: IP >> G6P > IHP (Table 4; Fig. 2). However, the trend was different for the adsorbed GLY compound, which, depending on the minerals, was in this order IP = GLY (goethite and montmorillonite) or in this order GLY >> IP (gibbsite). Thus, P uptake from GLY

Table 5

One-way ANOVA results testing the effects of OP compounds by soil minerals on total P uptake, P availability, and dry weight. Soils minerals (Go: goethite, Gib: gibbsite, K: kaolinite, and M: montmorillonite); OP: Organic Phosphorus.

Variables effects	P uptake <i>p</i> -value	P availability <i>p</i> -value	Dry weight <i>p</i> -value
Go-OP	< 0.001	< 0.001	0.07
Gib-OP	< 0.001	< 0.001	0.92
K-OP	0.05	< 0.05	0.08
M-OP	<0.001	< 0.01	0.72

adsorbed on goethite and montmorillonite was similar to the adsorbed IP compound while P uptake from GLY adsorbed on gibbsite was significantly higher than IP. Moreover, P uptake was highly variable and strongly dependent on the characteristics of the OP compounds. Successive desorption of the different mineral-P complexes with KCl (see supplementary data Fig. S1) also indicated that, in general, the percentage of OP desorption at all cycles was in the order GLY >> G6P > IHP, which was similar to the trend observed for OP availability and uptake by the plant (Fig. 2). In addition, the forms of P significantly impacted phosphatase activity in the rhizosphere (Fig. 3). Irrespective of the soil minerals, treatments might be ranked according to their phosphatase activity as follows: GLY >> G6P > IHP (Fig. 3). In sum, OP adsorbed on soil minerals was available to ryegrass since the plant was able to take up a certain amount of it even if it was relatively low from certain mineral-OP complexes, e.g., mineral-IHP complexes.

3.4. Relationships between P uptake, soil minerals-OP interaction and P availability

The P uptake was influenced by the soil mineral-OP interactions. Phosphorus uptake from OP adsorbed onto the four tested minerals increased in the following order: kaolinite-OP << gibbsite-OP ≤ goethite OP << montmorillonite-OP. A large difference was observed among kaolinite, Fe and Al oxyhydroxides and montmorillonite in their ability to release P for plant uptake (Fig. 2). The amount of P taken up from montmorillonite-OP complexes was the highest. On the other hand, P uptake from goethite-OP, gibbsite-OP, and kaolinite-OP (especially gib-IHP or G6P) was low. Overall, less than 4 % of the initial adsorbed P was desorbed and mineralized for plant uptake (Table 4).

Phosphorus uptake by ryegrass from mineral complexes was positively correlated with ΔP resin ($R = 0.73$, $p < 0.01$) (Fig. 4). However, no correlation was found between P uptake, resin-extracted P concentration in the rhizosphere (Resin P), and KCl-extractable P concentration. In addition, the ΔP resin values of the majority of the mineral-OP were generally negative (Fig. 5) even though some complexes, e.g., GLY-mineral complexes, showed almost nil ΔP resin values, i.e., no variation between resin P concentration in bulk soil and resin P concentration in the rhizosphere (Fig. 5).

4. Discussion

4.1. Phosphorus from adsorbed OP compounds is available to plants

Our first hypothesis that P from adsorbed OP compounds is available to ryegrass and varies with soil mineral properties was confirmed in our experiment. The two main findings supporting the hypothesis are: (i) the ryegrass was able to take up about 3–18 % of OP adsorbed to soil minerals; (ii) OP compounds as well as their interactions with soil minerals significantly affected P uptake for ryegrass.

The amount of P recovered by ryegrass reached 5 % from adsorbed IHP, 9 % from G6P and 18 % from adsorbed GLY (Table 4). In general, P uptake decreased in the order GLY >> G6P > IHP. Taken together, these results indicate that, irrespective of the soil mineral, adsorbed OP was at least partially available to plants. The magnitude of this availability depended on the OP compounds and the types of soil minerals. By comparing several of the main soil mineral-OP complexes, our work indicates that some amount of P can be available from the adsorbed OP compounds demonstrating, therefore that adsorbed OPs can act as a source of P for plants.

The availability of P from adsorbed OP differed between OP compounds. The P uptake from the adsorbed GLY compound was much higher than that of adsorbed G6P which was more available than adsorbed IHP. It appears that the difference in availability between adsorbed OP compounds was determined by the adsorption/desorption capacity more than their binding strength. The trend in availability (GLY >> G6P > IHP) would be mainly explained by the distinct desorption

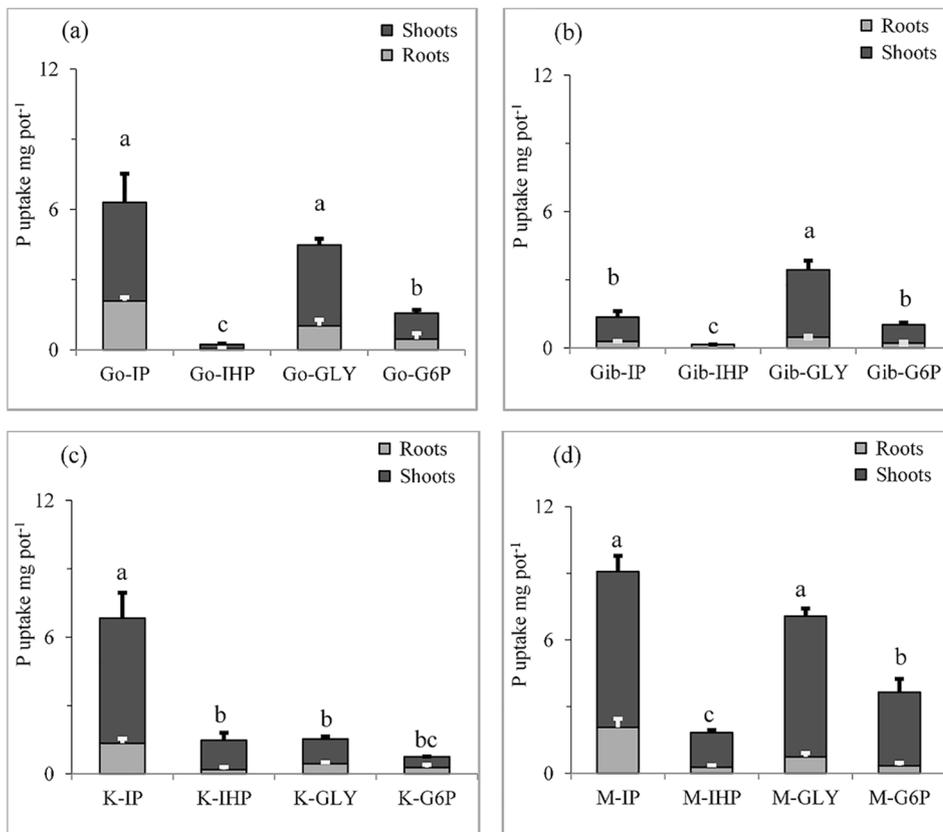


Fig. 2. Phosphorus uptake by root and shoot ryegrass plants with different P sources. The effect of P compounds, soil minerals, and their combined effect on total P uptake was significant ($P < 0.0001$) according to GLM model results testing the impact of factors (P compounds, soil minerals, and their combined effect) on total P uptake. Means with different letters were significantly different according to Tukey's HSD test at $P < 0.05$. Error bars indicate standard error. Soils minerals (Go: goethite, Gib: gibbsite, K: kaolinite, and M: montmorillonite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate and IP: KH_2PO_4); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

dynamics of the different minerals, leading to the lowest desorption for IHP-P, followed by G6P-P and then GLY-P (Amadou et al., 2022). This is also corroborated by the results of desorption dynamics (see supplementary data Fig S1). Yan et al. (2014) similarly showed lower desorption of IHP from different structures of aluminum (oxyhydr)oxides compared to other OP compounds. In addition, the trend in availability ($\text{GLY} \gg \text{G6P} > \text{IHP}$) could also be related to their different degrees of hydrolysis by enzymatic activity (Annaheim et al., 2010; Bünemann, 2008) as phosphatase activity was the highest in the presence of GLY and the lowest in the presence of IHP (Fig. 3). Basically, we expected G6P to be more available than GLY due to its higher desorption and its likely instability on soil minerals due to its higher molecular weight than GLY (Annaheim et al., 2013; Park et al., 2022; Yan et al., 2014). The opposite result we found may be the consequence of its more negatively charged surface compared to GLY (Giaveno et al., 2008; Qin et al., 2020; Ruttenberg and Sulak, 2011). These reasons would also explain why the binding energy of G6P predicted from the Langmuir model is often higher than that of GLY or IP (Bai et al., 2021; Goebel et al., 2017). Finally, adsorbed GLY was the higher source of P for plant uptake compared to other compounds, consistently with Adams and Pate (1992). In conclusion, the availability of OPs for plant nutrition from organic inputs and soil would be determined by the stability of OP-mineral complexes or by their (de)sorption dynamics as well as their hydrolysis by enzymes.

4.2. Effect of mineral-OP interactions on P uptake by ryegrass.

The potential availability of P adsorbed by different minerals was strongly affected by mineral-OP interaction properties. Except for the IHP, the P uptake from OP forms increased in the following order: kaolinite-OP \ll gibbsite-OP \leq goethite OP \ll montmorillonite-OP (Tableau 4). Montmorillonite-OP complexes showed the highest P uptake, with a maximum of up to 18 %. On the other hand, P uptake from

kaolinite-OP was the lowest. Less than 4 % of the initially adsorbed P was desorbed and mineralized for plant uptake. These results indicated that regardless of the type of mineral and its OP sorption strength and stability, plants are able to take up at least a small portion of it for their nutrition. This agrees with laboratory and greenhouse studies indicating that specifically adsorbed P was potentially available to plants although it was very difficult to desorb (Bollyn et al., 2017; D'Amico et al., 2020; Montalvo et al., 2015). Even under conditions where the root-associated microbiomes that can help mobilize P are limited, OP-mineral complexes still have potential for supplying P to plants.

Montmorillonite-OP complexes, in particular, montmorillonite-GLY or G6P were found to serve as sources of P in soils more than the other complexes. Organic P adsorbed on kaolinite released the lowest amount of P to the plants. Overall, there was a marked difference in P uptake between the tested minerals. Montmorillonite-OP complexes would provide more P due to the negative charges of montmorillonite (He et al., 1994) causing its weak binding to OP, resulting in the formation of unstable OP-montmorillonite complexes (He and Zhu, 1998; He et al., 1994; Hingston et al., 1974; Lang et al., 2017). The low P uptake from kaolinite-OP agrees with previous observations showing that kaolinite-P is an inner-sphere surface and bidentate complex below pH 6 (Hu et al., 2020; Ruyter-Hooley et al., 2015), and the adsorbed P on kaolinite is difficult to desorb (Kafkafi et al., 1988; Manning and Goldberg, 1996; Xiong et al., 2022). Hence, our result emphasized that Fe and Al oxyhydroxides were less responsible for limiting OP availability than kaolinite despite their general higher adsorption capacity in soil. Apart from the nature of the OP compounds, the characteristic of the minerals are an important factor responsible for the difference in P uptake between the tested OP-mineral complexes. Thus, it is important to further quantify the interaction of OP with soil minerals in order to characterize and subsequently model P availability.

No correlation was found between P uptake and resin-extracted P (Fig. 4). In addition, rhizosheath resin P concentration for most mineral-

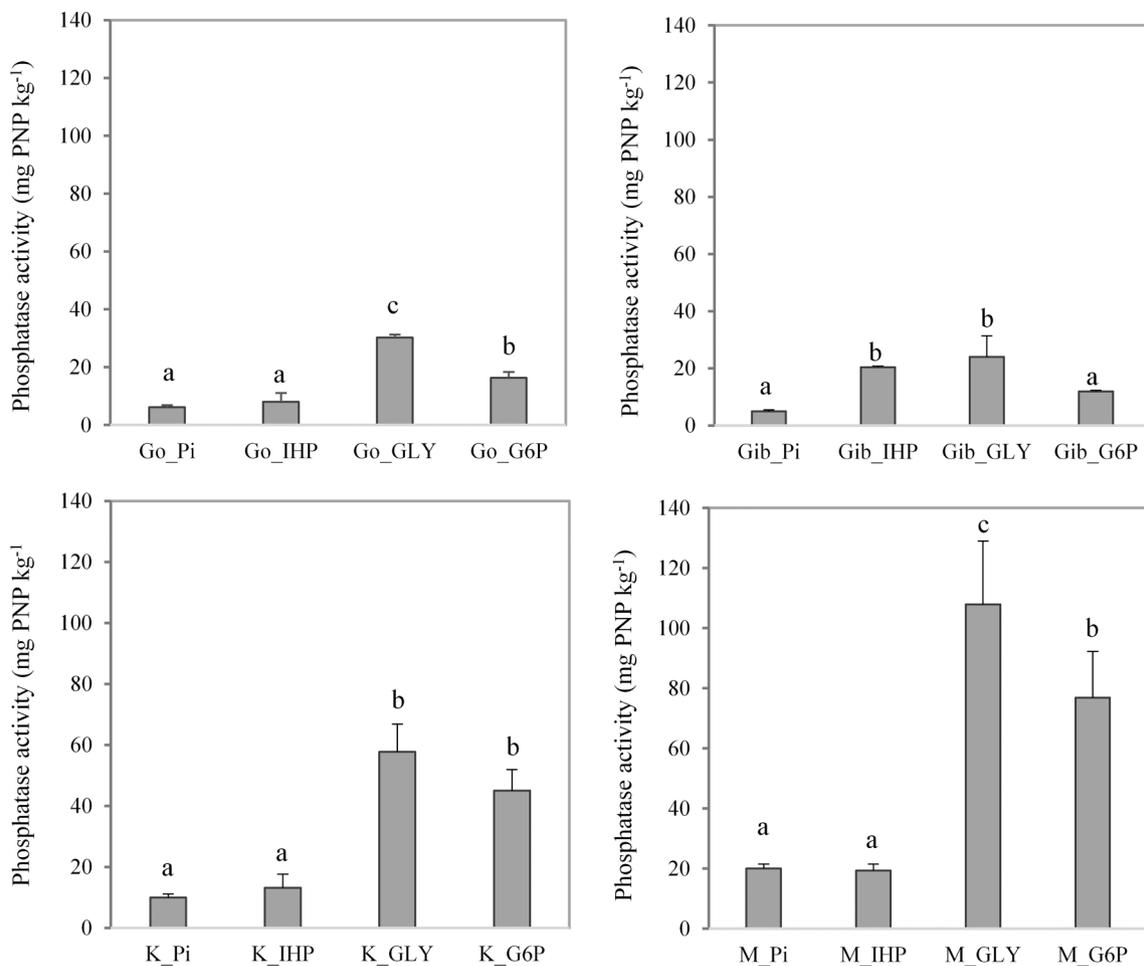


Fig. 3. Phosphatase activity in the rhizosphere at the end of the experiment. Means with different letters were significantly different according to the Tukey's HSD test at $P < 0.05$. Error bars indicate standard error. Soils minerals (Go: goethite, Gib: gibbsite, K: kaolinite, and M: montmorillonite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate and IP: KH_2PO_4); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

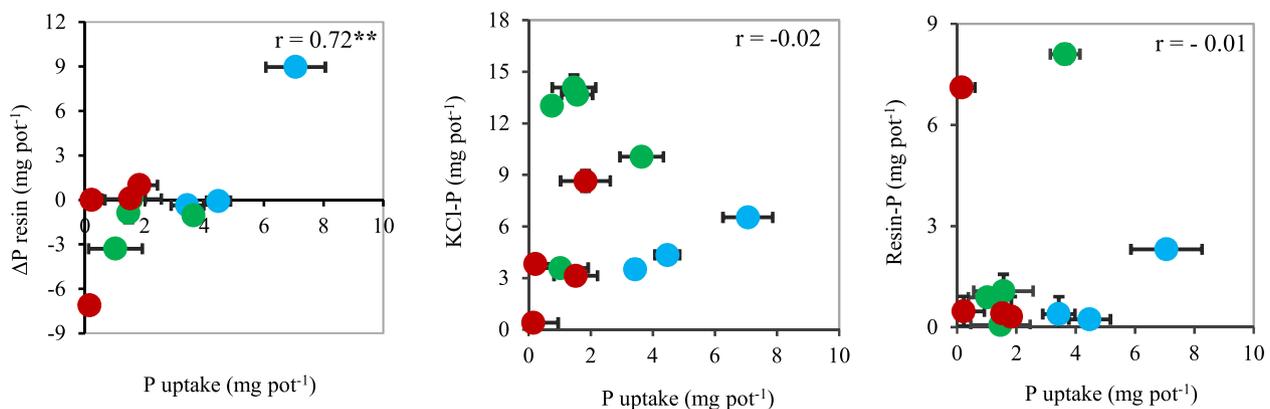


Fig. 4. Relationship between P uptake and the different methods of P extraction (ΔP resin: difference in resin P concentration between bulk soil and rhizosphere. KCl-P: KCl extracted P). Values are average ($n = 4$) \pm standard deviations. The marked correlation coefficient r is the Pearson's correlation coefficient. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$. Dots colors distinguish the forms of P. Red dots correspond to myo-inositol hexakisphosphate (IHP), green to glucose-6-phosphate (G6P) and blue to glycerophosphate (GLY). Dots colors distinguish the forms of P. Red dots correspond to myo-inositol hexakisphosphate (IHP), green to glucose-6-phosphate (G6P) and blue to glycerophosphate (GLY).

OP complexes was higher than that of the bulk soil. These results suggest that plants have induced additional desorption of OP. According to Le Chatelier's principle (Law of Mass Action), the sink effect of roots caused an OP depletion in the solution, which in turn induced further OP

desorption dissolution to replenish the solution (Houben and Sonnet, 2012; Penn and Camberato, 2019). In addition, mobilization of OP by ryegrass roots might also have contributed to OP depletion. As shown by Martin et al. (2002), high efficiency of ryegrass in displacing strongly

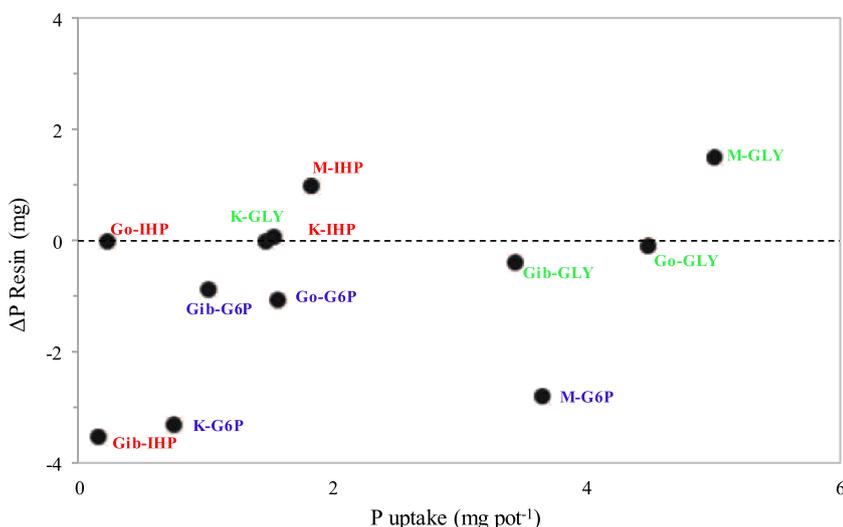


Fig. 5. Relationship between Δ resin P (difference in resin P concentration between bulk soil and rhizosphere) and P uptake. Soils minerals (Go: goethite, Gib: gibbsite, K: kaolinite and M: montmorillonite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate and IP: KH_2PO_4); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

bounded P may be due to the fact that the plant can react to P deficiency by extending the root surface and utilizing more than one mechanism of extraction at the same time. Thus, the effect of plant uptake may result in additional mobilization of OP forms from soil minerals.

It is generally accepted that P extraction with KCl is negatively correlated with the binding energy of the P compounds to soils. Thus, the more P can be extracted with KCl to become available to plants, the lower its binding energy (Martin et al., 2004; Yan et al., 2014). However, our results showed no correlation between P uptake and P extracted with KCl. The lack of correlation in our case may imply that the P taken up by plants did not depend on the strength or energy with which OP compounds are bounded to soil minerals. Nevertheless, this lack of correlation between P taken up by plants and P extracted by KCl could also mean that OP compounds may have been released from the soil minerals but remained in organic form without being mineralized for uptake by plants. Therefore, we hypothesize that although OP was desorbed from some minerals, it may not have been absorbed because it was not readily hydrolyzable by the enzyme released by plant roots. This supports our earlier explanation of the resistance of some of OP compounds to enzymatic hydrolysis because of their chemical properties. Therefore, the availability of adsorbed OPs to plants does not depend on their binding strength to soil minerals but rather on their degree of hydrolysis by soil and root enzymes.

Finally, P uptake by ryegrass was positively correlated with Δ P resin ($R = 0.73$, $p < 0.01$), suggesting that the variation of available P in the rhizosphere determined the P uptake by plant (Fig. 4). The Δ P resin values of the majority of the mineral-OP complexes were generally negative, showing that in addition to the spontaneously released P, there would have been a subsequent release of P from soil minerals that would occur in response to plant-induced depletion of available P in the rhizosphere. This means that plant roots mobilized additional P from minerals. However, this finding did not apply to all OP-minerals complexes. For instance, GLY-mineral complexes (Fig. 4) showed almost no variation in Δ P resin, i.e. no variation between P resin in the bulk soil and P resin in the rhizosphere, suggesting that plant absorbed only the spontaneously available P without any other mobilization. This confirms that GLY was sufficiently available from soil minerals. Thus, when the plant was in the presence of soil minerals associated with GLY, there was little or no additional P mobilization.

4.3. Phosphorus uptake from adsorbed OP relative to adsorbed IP

Our third hypothesis was that P derived from adsorbed OP would be less available than P derived from adsorbed IP because it desorbs less and requires also enzymatic cleavage before being taken up by ryegrass.

Our results support only partially this hypothesis as they showed that the different adsorbed OP compounds led to contrasted P uptake compared to the adsorbed IP compound. Phosphorus uptake from adsorbed IHP and G6P was significantly lower than that of adsorbed IP, whereas P uptake from adsorbed GLY, depending on the mineral, was slightly equal or higher than that of IP. Several studies have shown lower plant availability of adsorbed OP compounds compared to IP compounds (Andrino et al., 2019; D'Amico et al., 2020; Klotzbücher et al., 2019), probably due to the specific binding mechanisms of OP and its low desorption from soil (Bollyn et al., 2017; Ruyter-Hooley et al., 2015). However, in all of these studies, “organic P” refers only to IHP. In addition to IHP, GLY and G6P are also commonly found in soils, soils treated with organic inputs, sediments and wetlands (Missong et al., 2016; Vincent et al., 2013) but these OP forms have not been considered potential sources of P for plants, except in a few studies (Adams and Pate, 1992). Here, our results highlight the relative availability of these major OP forms compared to that of IP. In agreement with previous studies (Andrino et al., 2019; D'Amico et al., 2020; Ruttenberg and Sulak, 2011), IHP was less available than IP. Similar to IHP, we also found that adsorbed G6P was less available than IP. This would be due to the fact that, unlike IP, both IHP and G6P forms must be hydrolyzed after desorption to be available (D'Amico et al., 2020). In the present study, the phosphatase activity measured for IHP was very low compared to GLY, suggesting that the hydrolysis of IHP to an available IP form was very limited (Fig. 3). Finally, we found that the adsorbed GLY compound, depending on the minerals, was almost equivalent or more available than the IP compound. This high availability of GLY could be attributed to its low affinity for soil minerals and especially to its high desorption in soil. Soil amendment with organic inputs with high concentration of GLY would allow the efficient P fertilization from organic waste. This improving of knowledge on OP adsorption by soil minerals therefore reinforces the applications of OP for sustainable alternative to mineral P fertilizer. More importantly, we showed that on Al oxyhydroxides, GLY was significantly more available than IP. Thus, based on comparisons of different P compounds, our results showed that in soil, unlike IHP, another major compound of OP such as GLY can be equal or superior to IP in terms of plant availability.

5. Conclusion

Our results demonstrate that adsorbed OP compounds may be a source of P for plants irrespective of the type of mineral and its sorption capacity. Higher use efficiency of OP adsorbed on montmorillonite than on other minerals indicates that soils rich in 2:1 phyllosilicate might have greater P availability than soils rich in Fe and Al oxyhydroxides or

1:1 mineral. In addition, GLY would be less affected by Al oxyhydroxides that limit P availability in highly weathered soils in tropical regions. The binding strength of OPs to the mineral surface does not necessarily affect P availability to plants and plant uptake may result in additional P mobilization in the rhizosphere. Finally, the wide range of P uptake and availability in the presence of different mineral-OP complexes emphasized the importance of considering the chemical nature of OP and its ability to interact with soil minerals when attempting to improve soil OP cycling for plant use. As a further step, the role of OP-soil minerals interactions on P availability should be unraveled according to the main plant P acquisition strategies (e.g. mining, foraging and intermediates strategies) to design sustainable P cropping system.

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Author contributions

A. I. prepared and wrote the manuscript; D. H and M. P. defined the outline, main highlights, revisions and suggestions of the manuscript, tables and figures. All authors have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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